

Principles of — Polymerization —

SECOND EDITION

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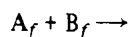
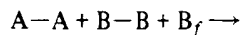
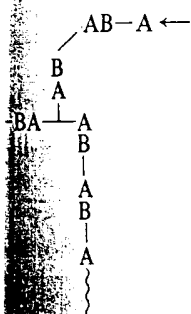
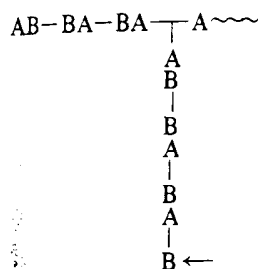
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Crosslinking is distinguished by the occurrence of *gelation* at some point in the polymerization. At this point, termed the *gel point*, one first observes the visible formation of a *gel* or *insoluble polymer fraction*. (The gel point is alternately taken as the point at which the system loses fluidity as measured by the failure of an air bubble to rise in it.) The gel is insoluble in all solvents at elevated temperatures under conditions where polymer degradation does not occur. The gel corresponds to the formation of an infinite network in which polymer molecules have been crosslinked to each other to form a macroscopic molecule. The gel is, in fact, considered as one molecule. The nongel portion of the polymer remains soluble in solvents. As the polymerization and gelation proceed beyond the gel point, the amount of gel increases at the expense of the sol as more and more polymer chains in the sol are crosslinked to the gel. There is a dramatic physical change that occurs during the process of gelation. The reaction mixture is transformed into a polymer of infinite viscosity.

The crosslinking reaction is an extremely important one from the commercial standpoint. Crosslinked plastics are increasingly used as engineering materials because of their excellent stability toward elevated temperatures and physical stress. They are dimensionally stable under a wide variety of conditions due to their rigid network structure. Such polymers will not flow when heated and are termed *thermosetting* polymers or simply *thermosets*. (Plastics that do soften and flow when heated, that is, uncrosslinked plastics, are called *thermoplastics*. Almost all of the polymers produced by chain polymerization are thermoplastics. There are only a relatively few such polymers which are crosslinked.) The commercial importance of the thermosets is seen from the fact that of the over 30 billion pounds of plastics produced annually in the United States, almost 5 billion pounds were crosslinked plastics [86,87].

In order to control the crosslinking reaction so that it can be used properly it is important to understand the relationship between gelation and the extent of reaction. Two general approaches have been used to relate the extent of reaction at the gel point to the composition of the polymerization system—based on calculating when \bar{X}_n and \bar{X}_w , respectively, reach the limit of infinite size.

2-10a Carothers Equation: $\bar{X}_n \rightarrow \infty$

2-10a-1 Equivalent Amounts of Reactants

Carothers derived a relationship between the extent of reaction at the gel point and the *average functionality* f_{avg} of the polymerization system for the case where the two functional groups A and B are present in equivalent amounts [16]. The derivation follows in a manner very close to that for Eq. 2-90. The average functionality of a mixture of monomers is the average number of functional groups per monomer molecule for all types of monomer molecules. It is defined by

droplets, for example, hydroxyapatite, barium sulfate, kaolin, and magnesium silicates. The initiators used are soluble in the monomer droplets. Such catalysts are often referred to as *oil-soluble initiators*. Each monomer droplet in a suspension is considered to be a small bulk polymerization system. The kinetics of polymerization within each droplet are the same as those for the corresponding bulk polymerization. The suspension method is not used with monomers which are highly soluble in water or whose polymer has too high a glass transition temperature. For appreciably water-soluble monomers, polymerization will take place in solution as well as in the monomer droplets with the former yielding appreciably lower molecular weights. Coagulation of the monomer droplets may occur at low conversions if the polymer T_g is lower than the polymerization temperature.

Dispersion polymerization, in which water is still the continuous phase, is a variation of suspension polymerization. The initiators and dispersants used are water-soluble ($>1\%$) in dispersion polymerization, while those in suspension polymerization are water-insoluble ($<1\%$). The water-soluble dispersants are generally organic polymers such as gelatin, methyl cellulose, poly(vinyl alcohol), and alkali salts of poly(methacrylic acid), often together with inorganic electrolytes. (The reader is cautioned that dispersion polymerizations are often referred to as suspension polymerizations.)

Heat and viscosity control in suspension and dispersion polymerization is relatively easy compared to bulk polymerization. Dispersion polymerization (and emulsion polymerization; Chap. 4) are of special value in producing finely divided, stable latexes and dispersions, which can be used directly as coatings, paints (the commonly encountered water-based paints), adhesives, and other products but are not as useful for producing high purity products free of the dispersants and other additives. Suspension polymers are more useful for this purpose since larger particles are produced and these can be (simply) isolated and purified by methods such as filtration and centrifugation. In recent years dispersion polymerizations using organic media as the continuous phase has become of interest as a means of directly producing organic-based paint and coating formulations. These polymerizations, usually involving a monomer and initiator dissolved in an organic solvent to produce insoluble polymer dispersed in the continuous phase (usually in the presence of a polymeric dispersant), are often referred to as *inverse dispersion polymerizations*.

3-13a-4 Other Processes

Polymerization of monomers in the solid and liquid-crystalline states, and in canal complexes [275], although studied in the laboratory, are not presently employed on a commercial scale.

3-13b Specific Commercial Polymers

3-13b-1 Polyethylene

Polymerization of ethylene to polyethylene [278-281,284,285] is carried out at



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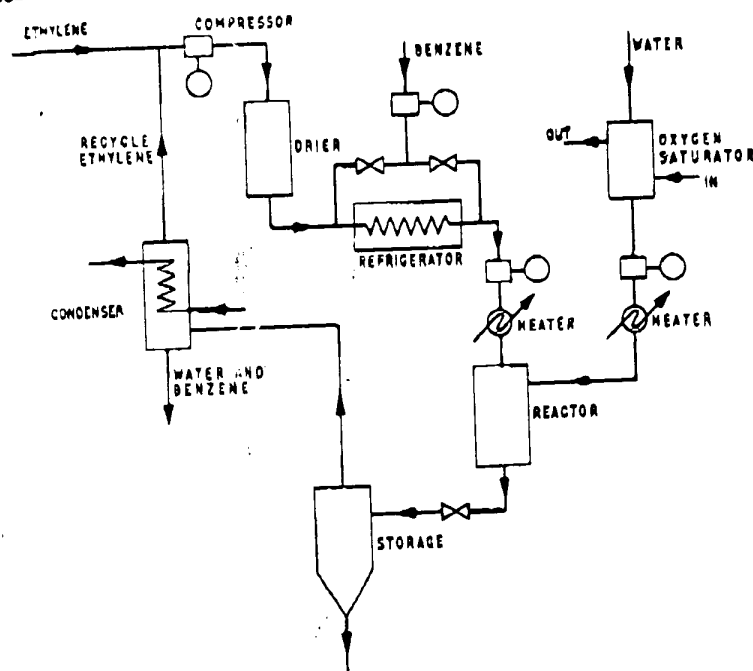


Fig. 3-22 Flow diagram of bulk high pressure polyethylene process. After [285] from U.S. Pat. 2,328,138 (Dupont) (by permission of Iliffe Books Ltd., London).

high pressures of 100–300 MPa and at temperatures above the melting temperature of polyethylene (usually 170–200°C but as high as 250°C) (Fig. 3-22 [285]). Polymerization occurs in the highly compressed gas (which behaves much as a liquid, even though ethylene is above its critical temperature). The system is usually considered a homogeneous one both initially and later when the polymer is highly swollen by ethylene. Trace amounts (5–300 ppm) of oxygen are typically used as initiator. Initiation probably involves the formation of peroxides and/or hydroperoxides of ethylene followed by their decomposition at the high polymerization temperatures. Alkyl and acyl peroxides, hydroperoxides, and azo compounds have also been used. Water, benzene or other diluents are often added to aid in heat dissipation; the system can then be considered a solution polymerization. The diluent also acts as a vehicle for an initiator other than oxygen. Chain transfer agents such as alcohols and ketones may also be present to regulate the molecular weight.

Batch processes are generally not as useful as continuous processes. The long residence time in a batch process gives relatively poor reproducibility and control. Long-chain branching due to transfer to polymer becomes excessive with deleterious effects on the physical properties. Continuous processes allow better balance and control of the polymerization. Tubular reactors (less than 2–3 cm diameter but up to 60 m in length) with very high linear velocities at the higher pressures give reaction times of minutes or less. The conversion per pass is low (15–30%), but the

overall process is rapid and economical. The polymer is separated from the gas and/or liquid phases at the end of each pass and ethylene monomer recycled after purification. The polymer is usually extruded into a ribbon and chopped up or granulated. The process may involve multiple additions of monomer, initiator, and chain transfer agents along the tube length. Tower and autoclave reactors are also employed. The product number-average molecular weight is generally in the range 20,000-50,000 with \bar{M}_w/\bar{M}_n being in the range 3-20 depending on process conditions.

Polyethylene (PE) has a wide range and combination of desirable properties. Its very low T_g of about -120°C , and moderately high T_m of about 135°C give it flexibility and utility over a wide temperature range. It has high crystallinity with a good combination of strength, flexibility, and melt-flow behavior over a range of molecular weights. The alkane structure of polyethylene imparts good solvent, chemical, thermal, oxidation, water, and electrical resistance. A wide range of fabrication techniques can be used to process polyethylene into products. This polyethylene is often referred to as *low-density polyethylene (LDPE)* or *high-pressure polyethylene* to distinguish it from the polyethylene synthesized at low pressures using coordination catalysts (Sec. 8-4e-2). The latter polyethylene is referred to as *low-pressure polyethylene* or *high-density polyethylene (HDPE)*. Low-density polyethylene is more highly branched (both long and short) than the latter and is therefore lower in crystallinity (50-70% vs 80-90%) and density ($0.91\text{--}0.93\text{ g/cm}^3$ vs $0.94\text{--}0.96\text{ g/cm}^3$). Almost 8 billion pounds per year of LDPE are produced in the United States [288a,b]. LDPE finds a wide range of applications as a flexible plastic [288c]. About 55% of all low-density polyethylene is produced as extruded film and sheet, mostly for packaging and household uses (bags, pouches and wrap for food, garments and dry cleaning, trash), but also for agricultural and construction applications (greenhouses, tank liners, moisture, and protective barriers). Injection molding of toys and housewares accounts for another 10-15%. About 15% or more of the LDPE produced is used in wire and cable insulation for power and communication transmission and extruded as well as hot melt coatings (on paper, metal foil, other plastic films). Other uses of LDPE include blow-molded bottles and containers, pipe, and tubing for agricultural irrigation.

Trade names for polyethylene include *Alathon*, *Hostalen*, *Marlex*, and *Petrothene*.

LDPE together with HDPE, polypropylene and other polymers of alkene (olefin) monomers comprise the *polyolefin* family of polymers. All except LDPE are produced by coordination catalysts.

3-13b-2 Polystyrene

Polymerization of styrene is carried out by the bulk and suspension processes (and



the emulsion process to a lesser extent). The heat dissipation problem in bulk

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